A Kinetic Feature of the Radiation-Induced Crosslinking Graft Polymerization of Various Monomers onto Polyethylene

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Bull. Inst. Chem. Res., Kyoto Univ., Vol. 56, No. 1, 1978

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Received January 11, 1978

The radiation-induced graft polymerizations of various monomers were studied in gas phase onto polyethylene and onto butadiene or isoprene pre-grafted polyethylene. Crosslinking of polyethylene took place simultaneously with the grafting. The graft polymerization rates of VCl and CTFE increased with reaction time in early stage of the reaction. The specific rate of graft polymerization, k_g=R/[M], was in the order, methyl methacrylate (MMA)>styrene (St)>methyl acrylate (MA)>vinyl acetate (VAc)>vinyl chloride (VCl)>chlorotrifluoroethylene (CTFE). The specific rate increased with the increasing monomer reactivity in the addition of polyethylene radical to monomer and with the decreasing ones in the reactions of chain transfer to monomer and termination. The rate ratio of graft polymerizations onto diene pre-grafted polyethylene and onto original one was in the order, MMA>St>MA>CTFE>VAc>VCl. While, gel fraction of the polymer obtained in the graft polymerization onto diene pre-grafted polyethylene was higher than that onto original one. The efficiency of grafted monomer for crosslinking was in the order, CTFE>VCl>VAc>MA>St>MMA. This efficiency was remarkably high in the graft polymerization of CTFE, VCl, and VAc onto diene pre-grafted polyethylene. The effects of unsaturations contained in polyethylene on the rate of grafting and the degree of gel formation of polymer were discussed in connection with the reactivities of propagating radicals to the unsaturations and of the monomers to polyethylene radical.

INTRODUCTION

Many works[1~5] on the radiation-induced graft polymerization of various monomers onto polyethylene have been carried out in order to improve the physical properties of the material and to elucidate the effect of reaction conditions on the graft polymerization. Little attention, however, have been paid to the characteristic features of the rates of grafting and crosslinking in connection with monomer reactivity and the elementary reaction of the grafting.

The purpose of this work is to elucidate the relation between the monomer reactivity and grafting rate, crosslinking rate, and kinetic features. Radiation-induced in-source crosslinking graft polymerization of various monomers, such as methyl methacrylate (MMA), styrene (St), methyl acrylate (MA), vinyl acetate (VAc), vinyl chloride (VCl) and chlorotrifluoroethylene (CTFE) onto polyethylene and diene pre-grafted polyethylene in gas phase were carried out.

On the basis of the experimental results, the characteristic features of grafting rate, crosslinking rate and kinetic behavior, and the effect of unsaturation groups

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contained in polyethylene on these features were discussed in connection with the considerations of the elementary reaction and the monomer reactivity.

EXPERIMENTAL

GR-grade of St, MMA, VAc, MA, and Ip were obtained commercially from Nakarai Chemical Co. Ltd., pure grade Bd and VCl, respectively, from Seitetsu Chemical Co. Ltd., and from Takachiho Chemical Co. Ltd., and CTFE was supplied from Daikin Kogyo Co. Ltd. Films (thickness, 20 μ) of low density polyethylene (Sumikathene; density, 0.92) and high density one (Hizex; density, 0.96) were used in the experiment.

Polyethylene film was placed in a glass ampule. Gaseous monomer was introduced into the ampule under the gas pressure of 1 atm after evacuation. Then, the ampule was sealed off under cooling the bottom of the ampule in liquid nitrogen. Whereas, with the use of liquid monomers, monomer and polyethylene film were placed in different ampules in a polymerization equipment of a letter 'H' in shape, which was made by connecting two glass ampules with a short glass tube. The liquid monomer was degassed five times through freezing-pumping-thawing cycles using vacuum line, and then sealed off under vacuum.

The ampule was irradiated with a cobalt 60 source at the dose rate of 0.05 Mrad/hr at room temperature. After the irradiation was stopped, the surface of the sample was wiped with a soft cloth, extracted with acetone for 10 hours in a Soxhlet extractor, dried under vacuum at 40°C for 10 hours before weighing.

In order to measure gel fraction, the film obtained was packed in a 100 mesh stainless steel basket, extracted with hot p-xylene in a Soxhlet extractor for 48 hours, washed with acetone for 4 hours in the same type extractor, dried in vacuum for 20 hours at 40°C and then weighed.

RESULTS AND DISCUSSION

1. Crosslinking Graft Polymerization of Various Monomers onto Polyethylene and onto Diene Pre-Grafted Polyethylene

Both the degree of grafting and the gel fraction of the polymer in the irradiation with 2.5 Mrad depend on the kinds of monomers and polyethylenes, as shown in Table I. The degree of grafting (mol/g-PE) is in the following order, MMA>MA$\simeq$St $\simeq$VCl>VAc>CTFE onto original polyethylene, and MMA>St>MA>VCl$\simeq$VAc $\geq$CTFE onto diene pre-grafted polyethylene. The degree of grafting of most of monomers onto low density polyethylene are higher (1.1–3.0 times) than those onto high density polyethylene, while that of CTFE onto low density polyethylene is lower (0.5 times) than that onto high density polyethylene.

The degrees of grafting of MMA, St, and MA onto diene pre-grafted polyethylene do not differ from those onto original one too greatly, while those of VCl, VAc, and CTFE onto diene pre-grafted polyethylene are smaller (0.5–0.02 times) than those onto original polyethylene.

On the other hand, the irradiation in the presence of various monomers except

Table I. Crosslinking Graft Polymerization of Various Monomers onto Polyethylene and Butadiene or Isoprene Pre-Grafted Polyethylene at a Dose of 2.5 Mrad at Room Temperature

Monomer	Polyethylene*3	Degree of grafting (wt%)	Degree of grafting (mol/g-PE)	Gel fraction*4 (wt%)	GF/DG*5 (%, g-PE/mol)
St*1	HDPE	115.8	0.0111	8.2	7.4×10^2
	LDPE	125.3	0.0120	6.4	5.7×10^2
	BG–LDPE	178.7	0.0172	74.0	4.3×10^3
	IG–LDPE	174.1	0.0167	76.6	4.6×10^3
MMA*1	HDPE	98.9	0.0095	0	0.0
	LDPE	266.5	0.0317	0	0.0
	BG–LDPE	377.1	0.0438	24.9	5.7×10^2
	IG–LDPE	368.0	0.0427	26.1	6.1×10^2
MA*1	HDPE	138.3	0.0161	69.9	4.3×10^3
	LDPE	129.5	0.0150	67.2	4.5×10^3
	BG–LDPE	97.4	0.0113	74.9	6.6×10^3
	IG–LDPE	87.1	0.0101	71.5	7.1×10^3
VAc*1	HDPE	47.3	0.0055	26.1	4.7×10^3
	LDPE	58.9	0.0068	17.7	2.6×10^3
	BG–LDPE	8.0	0.0009	44.6	4.8×10^4
	IG–LDPE	5.8	0.0007	43.3	6.5×10^4
VCl*2	HDPE	52.7	0.0084	58.4	7.0×10^3
	LDPE	138.6	0.0222	73.4	3.3×10^3
	BG–LDPE	11.9	0.0019	68.8	3.6×10^4
	IG–LDPE	3.3	0.0005	45.2	8.4×10^4
CTFE*2	HDPE	47.7	0.0041	42.0	1.0×10^4
	LDPE	21.7	0.0019	50.4	2.7×10^4
	BG–LDPE	10.4	0.0009	74.1	8.3×10^4
	IG–LDPE	5.0	0.0004	66.4	1.5×10^5

*1 Grafting in vapor phase of liquid monomer

*2 Grafting in gaseous monomer

*3 LDPE; low density polyethylene.
HDPE; high density polyethylene.
BG–LDPE; butadiene pre-grafted low density polyethylene (degree of grafting of butadiene; 4.6%).
IG–LDPE; isoprene pre-grafted low density polyethylene (degree of grafting of isoprene; 6.5%).

*4 Gel fraction of polyethylene irradiated at 2.5 Mrad in vacuum; 0.0 wt% for LDPE, 6.3 wt% for HDPE.

*5 The ratio of gel fraction to degree of grafting.

MMA gave higher gel fraction of polyethylene than those in vacuum. And, with the use of the diene pre-grafted polyethylene, remarkably higher gel fraction was observed in the graft polymerization of all monomers except VCl.

In order to make the relation between the grafting and the crosslinking reactions clear, the ratio of gel fraction to degree of grafting was estimated as the following order, CTFE>VCl≥MA≃VAc>St>MMA, for original polyethylene, and CTFE>VCl≃

VAc>MA>St>MMA, for diene pre-grafted polyethylene. This order is inverse to the order of degree of grafting.

The remarkably high ratio of gel fraction to degree of grafting was obtained in the graft polymerization of CTFE, VAc, and VCl onto diene pre-grafted polyethylene and these values were over 10 times larger than those of the other monomers.

The monomers such as CTFE, VAc, and VCl, which gave the lower degree of grafting, brought about the higher ratio of gel fraction to degree of grafting. In addition, these monomers led to lowering the degree of grafting with the use of diene pre-grafted polyethylene. These results indicate that the propagating graft chain radicals of CTFE, VAc, and VCl with high reactivity are liable to react with unsaturation groups contained in polyethylene to result in increasing the gel fraction and decreasing the degree of grafting as discussed in section 3.

Figures 1 and 2, respectively, show the change in the degree of grafting of various monomers onto low density polyethylene with irradiation time and that of CTFE onto various polyethylenes. In the graft polymerizations of VCl and CTFE onto various kinds of polyethylenes, the rate acceleration with reaction time was observed in early stage. From the log-log plot of the degree of grafting against reaction time, the time exponents of the degree of grafting are found to be 1.4–1.6 for CTFE graft polymerization onto various polyethylenes and about 1.2 for VCl. This indicates the existence of long lived radicals in these graft polymerizations as reported in the homopolymerizations of these monomers in bulk.[6,7]

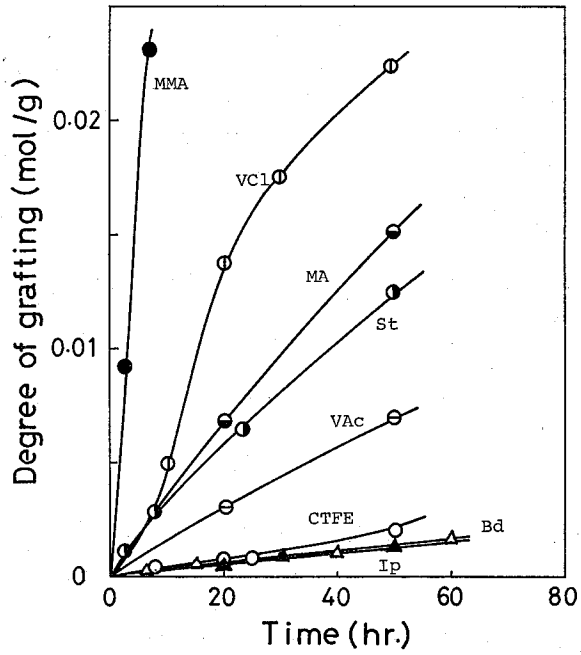


Fig. 1. Degree of grafting against irradiation time in the graft polymerization of various monomers onto low density polyethylene.

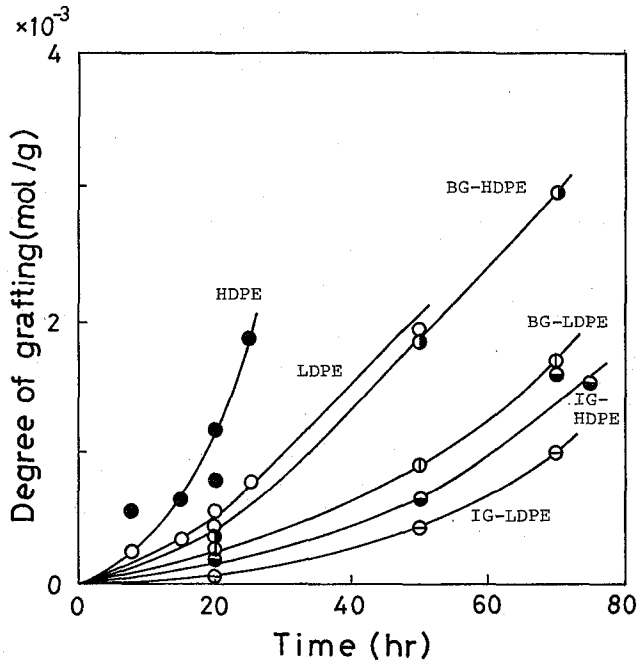


Fig. 2. Degree of grafting against irradiation time in the graft polymerization of CTFE onto various kinds of polyethylenes.

2. Relation between the Graft Polymerization Rate and the Monomer Reactivity

The specific rate, k_g, of the graft polymerization of various monomers was calculated from the following equation;

$$k_g = R/[M] \tag{1}$$

Here, R (mol/g-PE, hr) is the initial rate of graft polymerization and [M] (mol/l) is monomer concentration calculated from the vapor pressure of monomers. As is listed in Table II, the k_g value in graft polymerization onto original polyethylene is in the following order, MMA>St>MA>VAc>VCl>Ip≥CTFE≃Bd. This order does not agree with the order of the homopolymerization rate of these monomers.

In order to give an explanation for the order of the k_g values of these monomers, the following consideration was made in connection with the monomer reactivity in each elementary reaction of the graft polymerization.

The rate equation for each elementary reaction composed of the radiation-induced graft polymerization onto polyethylene can be written as follows;

Initiation

$$P \rightsquigarrow R\cdot \qquad R_d = k_d f I[P] \tag{2}$$

$$R\cdot + M \longrightarrow M\cdot \qquad R_i = k_i[R\cdot][M] \tag{3}$$

Propagation

$$M\cdot + M \longrightarrow M\cdot \qquad R_p = k_p[M\cdot][M] \tag{4}$$

Table II. Specific Rate of Graft Polymerization, k_g, Rate Constants, k_p, k_t, k_{trm}, for Each Elementary Reaction in Homopolymerization at 60°C, and Activation Energy of the Initiation Reaction (3), E_i.

Monomer	k_g (1/g-PE, hr) LDPE	HDPE	k_p (1/mol, sec)	k_t (1/mol, sec) $\times 10^{-6}$	k_{trm} (1/mol, sec)*1	E_i (kcal/mol)*2
MMA	1.260	0.511	734	37	0.0073	1.60
St	0.463	0.321	176	72	0.011	1.68
MA	0.073	0.078	2090	9.5	0.0067	1.83
VAc	0.028	0.023	3700	117	0.93	2.84
VCl	0.015	0.007	11000	2100	13.5	2.53
CTFE	0.001	0.001	—	—	—	—
Bd	0.001	0.001	—	—	—	—
Ip	0.001	0.002	—	—	—	—

*1 calculated from the values of transfer constant to monomer, Cm, and k_p reported in literature[8]

*2 calculated from equation (10) for the model reaction (9), D_π was used the value reported by Kagiya *et al.*[9] and D_σ was assumed to be equal to the bond dissociation energy of $(CH_3)_2CH-CH_3$ (74.5 kcal/mol).[10]

Chain transfer to polymer

$$M\cdot + P \longrightarrow P' + R\cdot \qquad R_{trp} = k_{trp}[M\cdot][P] \tag{5}$$

Chain transfer to monomer

$$M\cdot + M \longrightarrow P' + M\cdot' \qquad R_{trm} = k_{trm}[M\cdot][M] \tag{6}$$

Termination

$$M\cdot + M\cdot \longrightarrow P' \text{ or } 2P' \qquad R_t = k_t[M\cdot]^2 \tag{7}$$

Where P; polyethylene, P'; grafted polymer, M; monomer, R·; polyethylene radical, M·; propagating graft chain radical and M·'; monomer radical, respectively. The symbols k_d, k_i, k_p, k_{trp}, k_{trm} and k_t are the rate constants for each elementary reaction, f is the efficiency for the initiation of polyethylene radical, and I is the dose rate.

Assuming the steady state for the concentrations of radicals, R· and M·, the specific rate of graft polymerization can be expressed as follows;

$$\log k_g = \log k_p + \log \{\sqrt{(k_{trm}[M])^2 + 2k_d k_t f I[P]} - k_{trm}[M]\} - \log k_t \tag{8}$$

In the above formulation, radical M·' was not taken account as active radical for the grafting, because the radical can only initiate the homopolymerization. Equation (8) indicates that the specific rate of graft polymerization increases with the increase in k_p and with the decrease in k_t and k_{trm}.

Table II shows the values of k_g obtained in the graft polymerization onto original polyethylene, the rate constant for each elementary reaction, k_p, k_t, and k_{trm} reported in the homopolymerization of each monomer,[8] and the activation energy of the initiation reaction (3). As can be seen in this table and in Fig. 3, the k_g value increases with the decrease in k_t and k_{trm}, while decreases in spite of the increase in k_p. These facts indicate that the decreases in the rates of termination and transfer to monomer give the increase in the rate of graft polymerization, but the propagation reaction does not play an important role in the graft polymerization.

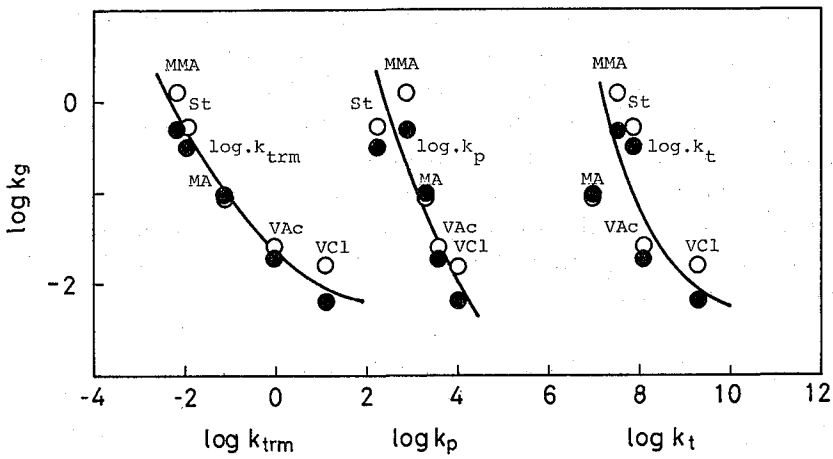


Fig. 3. Log-log plots of the specific rate of graft polymerization, k_g, against k_p, k_t, and k_{trm} in homopolymerization.
Symbols: (○) k_g onto low density polyethylene and (●) k_g onto high density polyethylene.

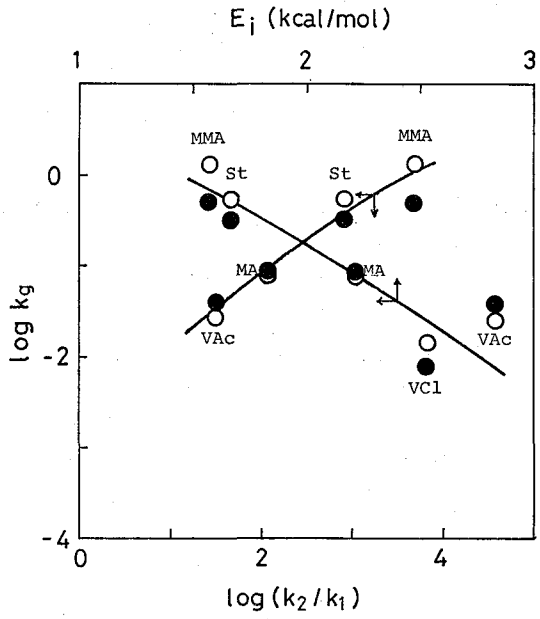


Fig. 4. Plots of log k_g against the logarithm of monomer reactivity to methyl radical, k_2/k_1,* and the activation energy of initiation, E_i. Symbols are the same as in Fig. 3.
* k_1 and k_2 are the rate constants of the following reactions;

$$CH_3\cdot + SH \xrightarrow{k_1} CH_4 + S\cdot \quad (1)$$

$$CH_3\cdot + M \xrightarrow{k_2} CH_3M\cdot \quad (2)$$

where SH is *iso*-octane and M is monomer.[11]

In order to clarify the role of the reactions of monomer addition to polyethylene radical (initiation) in the graft polymerization, the k_g value plotted against the reactivities of monomers to methyl radical reported by Szwarc[11] (Fig. 4).

The fact that the k_g value in the graft polymerization increases with the increase in the reactivity of monomer to methyl radical indicates that the monomer addition reactions such as the initiation also play an important role in the graft polymerization as well as the reactions of chain transfer to monomer and termination.

The activation energy, E_i, for the initiation reaction can be estimated from the following model reaction;

$$CH_3\text{-}\dot{C}H\text{-}CH_3 + CH_2{=}CXY \longrightarrow (CH_3)_2CH\text{-}CH_2\overset{\overset{X}{|}}{\underset{\underset{Y}{|}}{C}}\cdot \qquad (9)$$

using the Eq. (10)

$$E_i = \frac{D_\pi[(1-2\kappa)D_f + \kappa^2 D_\pi]^2}{(D_f - \kappa^2 D_\pi)^2} \qquad (10)$$

where

$$\kappa = \exp(0.0280Q) \qquad (11)$$

reported by Kagiya *et al.*[9] Here, D_π and D_f are the dissociation energies of π-bond of monomer ($CH_2{=}CXY$) and σ-bond formed newly in the produced radical ($(CH_3)_2CH\text{–}CH_2C(XY)\cdot$). Q is the heat of reaction.

As can be also seen in Fig. 4, the k_g value increases with the decrease in the E_i value. This relation supports the consideration that the initiation is the rate determining elementary reaction in the graft polymerization.

3. Effect of Unsaturation Groups Contained in Polyethylene on the Crosslinking Graft Polymerization

With the use of the diene pre-grafted polyethylene, remarkable retardation of the grafting of VAc, VCl, and CTFE, and promotion of the gel formation of the polymers were observed in the grafting of all monomers, as was mentioned in section 1.

In order to elucidate the effect of unsaturation groups in polyethylene on the rate of graft polymerization, the ratio of the specific rate of graft polymerization of each monomer onto diene pre-grafted low density polyethylene (k_g(DG-LDPE)) and that onto original one (k_g(LDPE)) is plotted against the degree of pre-grafting of diene monomers (Fig. 5).

The ratio in the graft polymerization of MMA and St increased gradually with the increase in the degree of pre-grafting of dienes, while that of MA decreased slightly and those of VAc, VCl, and CTFE remarkably. It was found by IR-spectra of the resulted polymer that the amount of unsaturation groups, such as vinyl, vinylidene, and *trans*-vinylene, in diene pre-grafted polyethylene was decreased by the grafting of CTFE.[12]

From these results, it is considered that the reaction of the propagating graft chain radical with the unsaturation groups contained in diene pre-grafted polyethylene takes place to result in the crosslinking and brings about the changes in the rates of graft polymerization.

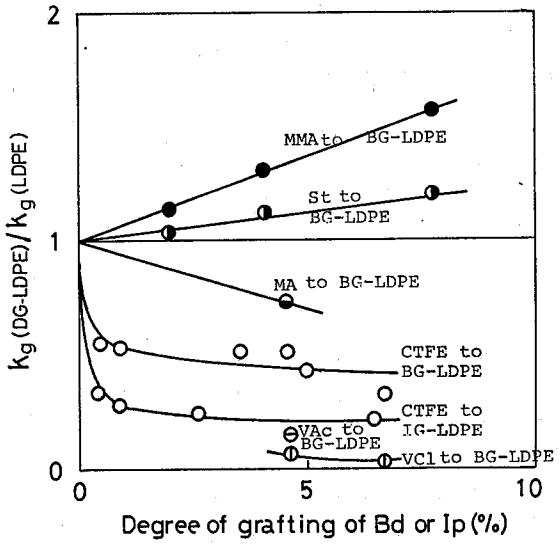
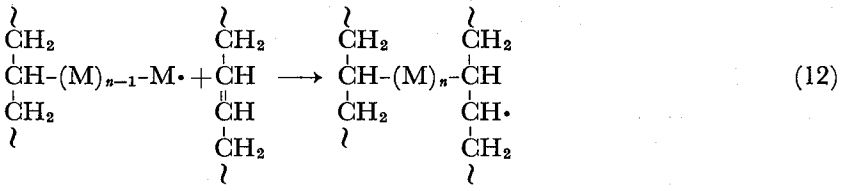


Fig. 5. Plot of k_g (DG-LDPE)/k_g(DLPE) against degree of grafting of butadiene or isoprene in diene pre-grafted polyethylene.

Three elementary reactions of the crosslinking with three types unsaturation groups contained in the polyethylene can be considered as shown below.



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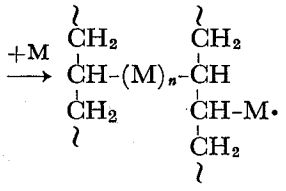

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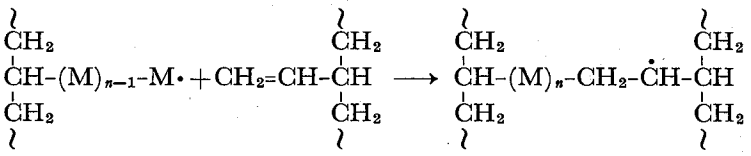

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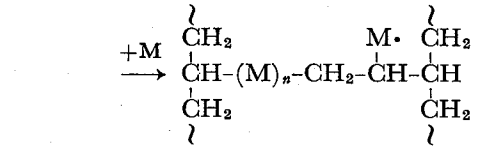

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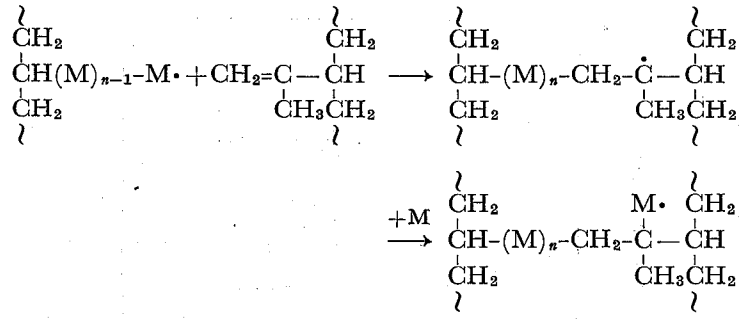


(16)

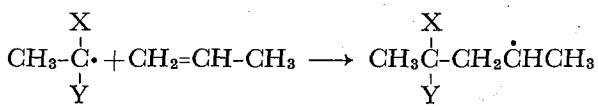
(17)

The above reactions are composed of the addition of propagating graft chain radical to various unsaturation groups (crosslinking; (12), (14), and (16)) and the monomer addition to the radical which is formed by crosslinking (reinitiation; (13), (15), and (17)).

In the graft polymerization, in which the crosslinking reaction is difficult to take place compared with the propagation, the grafting and the gel formation are not so much influenced by the unsaturation groups. If the crosslinking reaction is liable to take place and the reinitiation is slower than the propagation, the promotion of gel formation and the retardation of grafting should be observed. In order to discuss these problems, the following consideration was done in connection with the activation energy of each elementary reaction.

Figure 6 shows the relation between the ratio k_g(DG-PE)/k_g(PE) and the difference of activation energy of propagation, E_p, to that of addition of the propagating graft chain radical to the unsaturation groups (crosslinking), E_c.

E_c was calculated for the following model reaction;



(18)

using the dissociation energy of π-bond of propylene as 60.0 kcal/mol[9] and that of σ-bond newly formed in the resulted radical assumed to be equal to that of C–C σ–bond of monomers.

The crosslinking reaction occur parallel to the propagation. Therefore, the selectivity of the crosslinking reaction increases with the decrease in the value of E_c–E_p. As shown in Fig. 6, the ratio k_g(DG–PE)/k_g(PE) decreased with the decrease in E_c–E_p as expected.

While the rate of reinitiation is controlled by the activation energy E_i, because the reinitiation is practically the same reaction as the initiation. It was found that the ratio k_g(DG–PE)/k_g(PE) decreased with the increase in E_i (Fig. 6).

The monomers, such as VAc and VCl, with larger value of E_i have smaller E_c–E_p. Accordingly, the rates of graft polymerizations of these monomers decrease with the use of diene pre-grafted polyethylene. The reinitiation reactions in these graft polymerizations are the rate determining ones.

On the other hand, the degree of gel fraction in the graft polymerization of various monomers onto diene pre-grafted polyethylene varied also with the kinds of monomers (Table I). The efficiency of the grafted monomer for crosslinking can

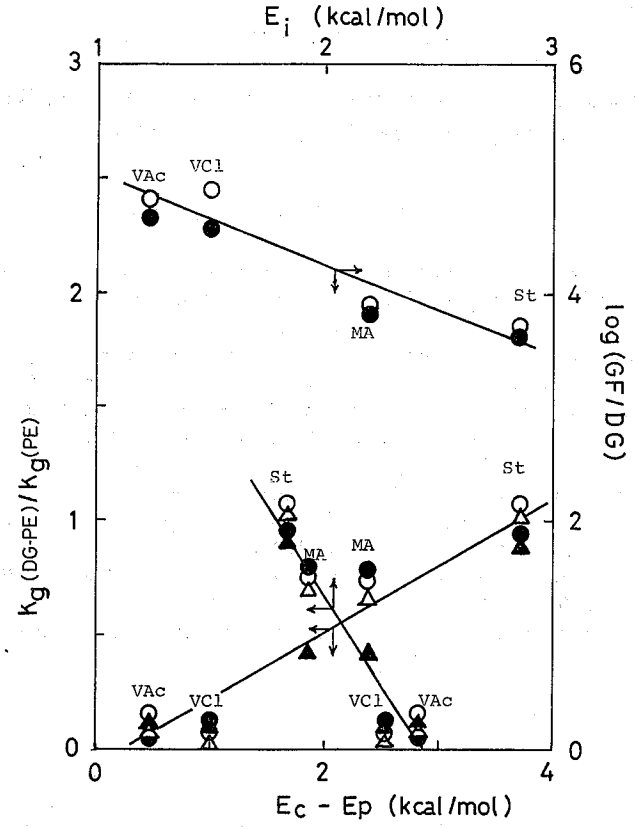


Fig. 6. Plots of the ratio k_g(DG–PE)/k_g(PE) and log (GF/DG) against E_c–E_p, and plot of the ratio k_g(DG–PE)/k_g(PE) against E_i.
Symbols: k_g(DG–PE)/k_g(PE); (○) k_g(BG–LDPE)/k_g(LDPE), (△) k_g(IG-LDPE)/k_g(LDPE), (●) k_g(BG–HDPE)/k_g(HDPE), (▲) k_g(IG–HDPE)/k_g(HDPE): GF/DG; (○) GF/DG in grafting onto BG–LDPE, (●) GF–DG in grafting onto IG–LDPE. Where, degree of grafting of diene in diene pre-grafted polyethylene; BG–LDPE, 4.6%; IG–LDPE, 6.7%; BG–HDPE, 5.0%, IG–LDPE, 6.5%.

be estimated as the ratio of the gel fraction to the degree of grafting (GF/DG). The values in the graft polymerization of various monomers onto diene pre-grafted polyethylene increased with the decrease in the difference of the activation energies E_c–E_p as can be seen in Fig. 6. This indicates that the graft polymerizations of the monomers showing high reactivity of the propagating graft chain radical to unsaturation groups give the higher efficiency for crosslinking.

These relations derived from the considerations of the elementary reaction mechanism and the activation energy of the reaction consist with the facts that with the use of diene pre-grafted polyethylene the graft polymerization of the monomer with lower value of E_c–E_p brought about the lower rate of grafting and the higher efficiency for the crosslinking.

The detailed study on the relative reactivity of various kinds of unsaturation groups in polyethylene in the crosslinking graft polymerization will be reported in subsequent paper.

ACKNOWLEDGMENT

The authors wish to thank the Institute for Chemical Research, Kyoto University for permitting us to use the Co-60 γ-ray irradiation apparatus.

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